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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF
COBALT.

SECOND PAPER:—THE DETERMINATION OF THE COBALT IN
COBALTOUS BROMIDE.

By THEODORE WILLIAM RICHARDS AND GREGORY PAUL BAXTER.

Presented October 12, 1898. Received December 29, 1898

IN a recent paper upon the atomic weight of cobalt,* we began the analysis of cobaltous bromide by the determination of its bromine, with results which seemed to show that the atomic weight of cobalt is very nearly 58.99 ($O = 16$). Although very great care was taken in purifying the cobaltous bromide used in this work, it was never certain that during the sublimation of the bromide in the porcelain tubes small amounts of impurity had not crept in. The situation here was exactly the same as in the research upon nickel, carried on at the same time in this Laboratory,† and here also the simplest and most convincing way of settling the question was to determine directly the amount of cobalt present in the salt, thus obtaining its total percentage composition.

Of the three methods of procedure which presented themselves,—precipitation, electrolysis, and reduction of the bromide,—reduction by hydrogen was chosen as being the least complicated and most certain. The slight hope offered in the nickel research that electrolysis might be used for the determination of the metal was here lacking on account of the greater difficulty in obtaining a satisfactory electrolytic deposit.

A conceivable objection to the use of the reduction of an *oxide* as an accurate quantitative method is the possibility that this reaction may not be capable of absolutely complete fulfilment. It is well known, for example, that one is rarely able to reoxidize wholly a metal once reduced,

* These Proceedings, XXXIII. 115.

† The preceding paper describes this work. This Volume, p. 327.

even if the material is finely divided. In the case of the oxide there is no means of deciding whether or not the last traces of oxygen have been removed, while in the case of the *bromide* a residue of halogen is easily detected. The complete reduction of nickelous bromide described in the preceding paper shows that some such operations are in fact possible. It is easy to see how the increase in volume involved in oxidation might cause a part of the metal to be permanently protected by the growing coat of oxide; on the other hand, an oxide or salt which is being reduced leaves only its skeleton behind, the innermost meshes of which may be penetrated by the reducing agent.

Cobaltous bromide when heated in a current of dry hydrogen begins to be reduced at a temperature of about 350° . At higher temperatures the reduction goes on more rapidly, but is then accompanied by partial sublimation of the bromide. Schützenberger's* observations on the sublimation of nickelous chloride were similar to these, but he seemed to think that some strange compound must have been the medium of the change, instead of realizing that in the presence of hydrochloric acid a trace of the vapor of the metallic salt might easily exist even in an atmosphere of hydrogen.

If the hydrogen is *moist*, however, the action begins at a lower temperature, about 250° ; but even under these conditions sublimation can be completely avoided only with the greatest difficulty. The reduction of *nickelous* bromide offered fewer difficulties; this process could be effected in a current of dry hydrogen, and without danger of sublimation of a trace of the material. The fact that moist hydrogen is more efficient than the dry gas is easily explained by the hypothesis that the oxide is formed as the first step in the reaction.

PURIFICATION OF MATERIALS.

Preparation of Cobaltous Bromide. — The cobaltous bromide used in this work was prepared by methods similar to those used in our previous investigation, and for details the previous paper should be consulted. Pure metallic cobalt was heated in a current of pure bromine and hydrobromic acid, and the sublimed bromide was preserved in weighing bottles contained in desiccators until used for analysis. Samples I. and II. were essentially the same as in the earlier investigation, even greater pains having been taken, however, in the purification of the reagents and water used in their preparation. Sample III. likewise was purified by

* Compt. Rend., CXIII. 177.

essentially the same method as before, but was then further treated by six additional recrystallizations as the purpureo-chloride, with the help of very pure redistilled ammonia and hydrochloric acid. The oxides obtained from these preparations were finally reduced by means of pure hydrogen, instead of by ammonia as before.

Preparation of Bromine. — Here also the process of purification did not differ from that previously employed. The purity of the bromine is sufficiently proven by two analyses in which a known weight of silver was precipitated by a slight excess of ammoniac bromide made from the halogen.

Ag in Vacuum. grams.	AgBr in Vacuum. grams.	AgBr : Ag
2.91386	5.07226	57.447
2.97097	5.17170	57.447
	Average	57.447
	Stas found	57.445

The balance and weights used in this work were the same as those described in our previous paper. The weights were carefully restandardized, the values differing from those previously found by only a few hundredths of a milligram. Since the balance was wholly free from iron, no inaccuracies could have arisen from magnetic attraction, either in this work or in that upon nickel.

Owing to the fact that the specific gravity of cobalt is almost identical with that of brass, no correction was required to reduce the weight of the cobalt to a vacuum standard.

The correction of +.00010 gram per gram of cobaltous bromide was applied in each case to the weighings of that material. All weighings were made by substitution, as usual.

We are indebted to the Cyrus M. Warren Fund for Chemical Research in Harvard University for some of our more expensive pieces of apparatus.

METHOD OF ANALYSIS.

By means of the glass apparatus described in our earlier paper, cobaltous bromide, contained in a platinum boat, was dried in a current of pure dry nitrogen and hydrobromic acid gas in a hard glass tube heated to about 400°; and after the tube had been thoroughly swept out with nitrogen and then by dry air, the boat was transferred to a weighing bottle in this safe atmosphere. The bottle was then weighed, and the

boat carefully placed in the reduction tube, where it was heated in a current of moist hydrogen until the fumes of hydrobromic acid ceased to come off. The tube was then swept out with dry hydrogen, and when cool the boat was quickly replaced in the weighing bottle containing dry air, and was thus weighed after a suitable delay. In most analyses this process was repeated until the weight of the cobalt ceased to change. Cobalt reduced from the bromide is less constant in weight than nickel, gaining several tenths of a milligram in weight in twenty-four hours.

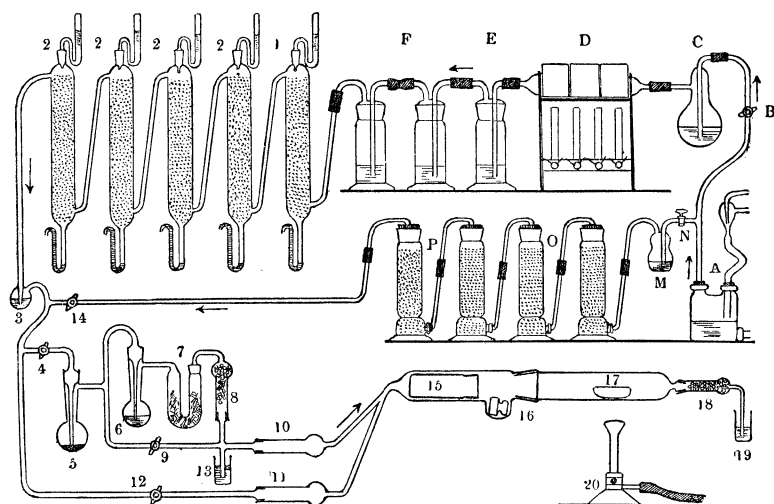


FIG. 1. APPARATUS FOR IGNITING COBALTOUS BROMIDE IN ANY DESIRED MIXTURE OF GASES.

The use of rubber was confined to the first part of this train, where it could do no harm (A B C D E F and A M N O P).

For this reason the metal was always allowed to become thoroughly cool in the atmosphere of hydrogen, and the weighing bottle was allowed to come to perfect equilibrium with the atmospheric conditions inside a desiccator at the room temperature before receiving the boat. After half an hour *nickel* treated in the same way had been found to come to constant weight, and in half an hour the opportunity for oxidation of cobalt is so slight as to be negligible; hence this interval was the one which always elapsed between the bottling and the weighing of the cobalt. In one analysis, to see if exposure to the air affected the weight of the cobalt, the boat was bottled in dry nitrogen in the bottling apparatus, after

being heated to constant weight in the usual way. Upon correcting the weight of the bottle for the difference in weight of nitrogen and air, the weights obtained by both methods agreed perfectly.

The resulting cobalt was in the form of a gray metallic sponge, which showed no traces of oxidation upon standing in air. Since previous work by other experimenters* is not unanimous as to the occlusion of hydrogen by cobalt under these circumstances, it seemed desirable to us to obtain more evidence on this point. Accordingly, in several analyses the boat containing the cobalt was placed in a hard glass tube sealed at one end. After the air had been exhausted by means of a Sprengel pump, the tube was heated to about 500°, the highest temperature used in the reduction. In no case was a measurable quantity of gas evolved, and the cobalt did not lose in weight; hence it would appear that cobalt prepared from the bromide does not possess the property of occluding important amounts of hydrogen when heated in the gas.

To avoid any possibility of error, two and a half grams of cobalt, freshly reduced from the bromide and allowed to cool in hydrogen, were subjected to quantitative combustion in the manner already described in the paper upon nickel. Only five tenths of a milligram of water were formed; and even the repeated reduction and combustion of the residual oxide yielded only a milligram. Evidently the amount of hydrogen occluded was very small. On the other hand, cobalt reduced originally from the oxide, when treated in the same way, was found to contain about fifteen times its volume of hydrogen and when allowed to remain in hydrogen several hours, it was found to have absorbed amounts comparable to those found by Neumann and Streintz.† A fuller statement of the experiments will be reserved for a future paper upon the nature and causes of these singular irregularities; for the present, it is sufficient to have shown that cobalt, like nickel, reduced from the bromide, does not retain enough hydrogen to vitiate the results recorded below.

It is perhaps worth while to state also that the empty platinum boat was tested as to its power of absorbing weighable amounts of hydrogen. After ignition and cooling in the gas, and bottling in dry air as usual, it was found to have gained 0.02 milligram when compared with its weight after ignition in air. Evidently the occlusion of hydrogen, if measurable at all, is balanced by adsorption of air; hence for our purpose it may be neglected.

* Neumann and Streintz, *Monatshefte für Chem.*, XII. 642; *Berichte d. d. ch. Gesell.*, XXV., 187R; Hempel and Thiele, *Zeitschr. Anorg. Chem.*, XI. 93.

† *Loc. cit.*

A slight sublimation of the cobaltous bromide took place during the reduction in almost every case. The amount of this sublimed material was determined by washing out the tube with a few cubic centimeters of nitric acid, and evaporating this liquid to dryness. After the solution of the residue in water and the addition of an excess of ammonia, a very dilute standard solution of potassic permanganate was run in until a pink color appeared. This method of Winkler's is applicable only when extremely small amounts of cobalt are present, because the brown color of the cobaltic salt interferes seriously with the end point in the presence of large amounts of cobalt. The weight of the cobaltous bromide thus sublimed never amounted to more than three tenths of a milligram, and seldom exceeded one tenth of a milligram.

The platinum boat used in the earlier work served to contain the bromide in these experiments also. Although the metallic cobalt alloyed itself with the surface of the boat to a slight extent, we were able to remove completely the alloy by treating the inside of the boat with aqua regia. After this treatment and scrubbing with round sand, the boat showed no trace of darkening upon ignition. Evidently, then, the cobalt had been completely removed. Of course a gradual loss of weight took place, owing to solution of small amounts of platinum, but this loss amounted to only half a gram in the course of the work.

In the first two determinations the hydrogen was generated from hydrochloric acid by means of pure zinc. It was purified by passing through bulbs containing silver nitrate, potash, silver nitrate again, then through a hard glass tube heated to redness. From this point the gas came in contact only with glass, being conducted through three towers containing glass beads moistened with silver nitrate, then by means of T-tubes, either directly in a moist state, or through a long drying tube containing stick potash, into the reduction tube. The reduction tube was connected with the rest of the apparatus by means of a ground glass joint.

A small amount of white sublimate, which appeared beyond the boat during each of the preliminary ignitions, proved to be ammonic bromide. The source of the ammonia was not at first apparent, as it was hard to believe that the cobaltous bromide could retain ammonic bromide at a temperature between 400° and 500°. Upon examination of the silver nitrate columns it was found that reduction had taken place there, metallic silver being precipitated upon the beads.* Of course the reduction of

* The fact that silver nitrate is reduced by molecular hydrogen has already been noted by other experimenters: Russell, *Jour. Chem. Soc.*, [2], XII. 3, (1874); Pellet, *Compt. Rend.*, LXXVIII. 1132.

the silver alone could do no harm; but unfortunately it was attended by a reduction of the nitric acid also. This was proved by passing the resulting gas through a hot tube, when traces of ammonia were formed, capable of easy detection by Nessler's reagent. We had come face to face with one of those frequent cases where an attempt at purification had introduced a flaw as serious as the one it eliminated. The very common use of argentic nitrate as a means of purifying hydrogen is obviously a pernicious one, if accurate results are desired.

The hydrogen apparatus was then entirely remodelled. Owing to the fact that the amount of hydrogen required for the completion of a reduction was very much larger than the amount actually necessary to combine with the bromine,* a gasometer was constructed which should collect the hydrogen after it had passed through the tube and deliver it repeatedly to the apparatus, after removal of the hydrobromic acid. The hydrogen was generated by a primary battery consisting of zinc amalgam, hydrochloric acid, and platinized platinum. The gas delivered by this apparatus is pure, except for the presence of a little hydrochloric acid, which can be removed easily by means of potash. The following cut shows the apparatus in its improved form.

The bottle *B* is filled with pure hydrogen generated by the battery *C*. From the bottle *A* water is siphoned into *B*, forcing the hydrogen by way of the stopcock *e* through the column *D*, filled with beads moistened with aqueous cupric sulphate to remove sulphur compounds taken from the rubber; through the columns *E* and *F* which contain dilute sodic hydrate, then either directly through *g* or through a potash tube *G* into the reduction tube *H*. After being freed from hydrobromic acid in the bottle *K* containing potash, the gas is conducted through the open stopcock *b* into *A*. When *B* is full of water the process can be repeated by interchanging *A* and *B*, and opening the stopcocks *c* and *d* after closing *b* and *e*. The generator *C* served to keep the pressure always outward. The current of gas could be regulated by a pinchcock *a* on the rubber siphon tube. This apparatus proved entirely satisfactory, and was not altered during the investigation.

As in the case of nickel, it was found impossible by reduction alone to remove the last traces of bromine from the spongy cobalt. Even long continued heating to a temperature much above the subliming point of cobaltous bromide failed to give complete reduction, the solutions of the reduced cobalt giving decided tests for bromine. In the first

* See the preceding paper, p. 333.

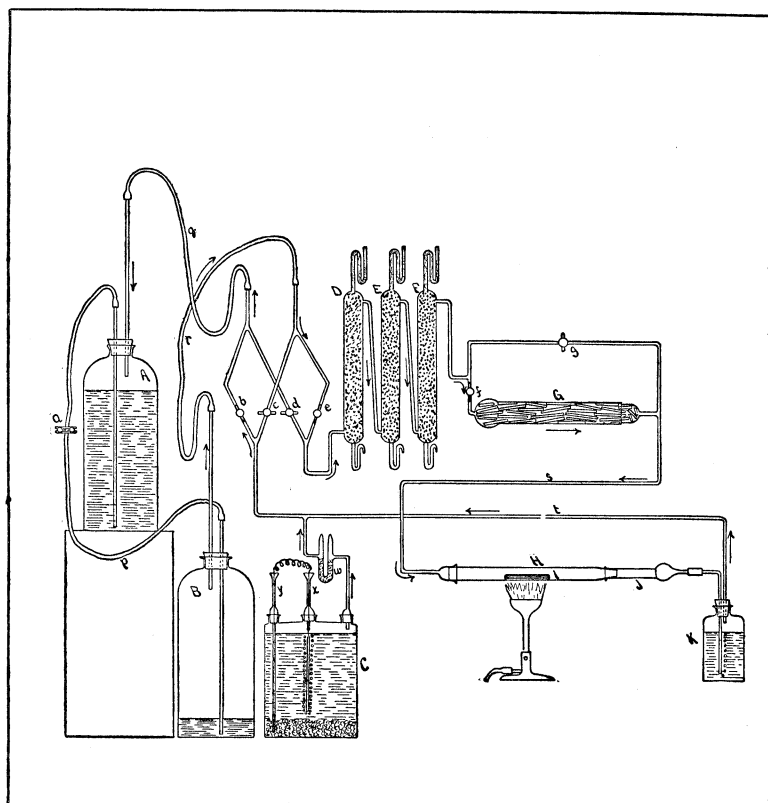


FIG. 2. APPARATUS FOR REDUCING THE BROMIDE.

analysis this bromine was precipitated with an excess of silver nitrate and weighed. In analyses 2, 3, and 4 the cobalt was leached with pure water, and after filtration the bromine was determined in the filtrate. The solutions of the cobalt in dilute nitric acid proved almost entirely free from bromine, that obtained from analysis 4 being entirely so. The silver bromide from these solutions was combined with that obtained from the aqueous extracts and weighed. As it was hard to believe that cobaltous bromide could be enclosed by the reduced cobalt in such a way as to remain unreduced and yet to go completely into solution with apparent ease, it was obvious that some foreign bromide must be present. Accordingly the filtrate from one of the precipitates of silver bromide

was treated with an excess of hydrobromic acid in order to remove the silver, and the refiltered solution was evaporated to dryness. Upon a careful qualitative analysis tests were obtained for nothing but sodium and traces of cobalt. The sodium evidently came from the porcelain tube used in the sublimation, and we were dealing with an impurity precisely similar in source and nature to that described in the case of nickelous bromide. As the two investigations progressed side by side, the discovery was almost simultaneous in the two cases. We have already said that this outcome was not an unexpected one.

Since it would be impossible to calculate the weight of the soluble bromides from the weight of the silver bromide without a quantitative analysis of the two bases present, the effort was made to evaporate the aqueous extract from the reduced cobalt and to weigh the dried residue directly. In the work upon nickel this method was necessarily rejected because the spongy nickel was oxidized and went into solution as nickelous hydrate which could not be removed by filtration. Our spongy cobalt oxidized much more rapidly than the nickel upon treatment with water; but the decantate, upon filtration and evaporation in the air, deposited most of its cobalt as cobaltic hydroxide. The presence of salts of the alkalis greatly increases this oxidation, cobalt which has once been leached being oxidized but little. Heat also increases the oxidation, and so probably does the galvanic action with the platinum dishes which were used wherever possible through the whole course of this investigation.

In view of the colloidal solubility of nickelous hydrate in water, it is probable that cobaltous hydrate possesses the same property. When cobalt is treated with water in the presence of air, the metal oxidizes and goes into solution as *cobaltous* hydrate; this is then further oxidized by exposure of the solution to the air and thrown out of solution as *cobaltic* hydrate, which can be filtered off. Since the dissolved cobalt is almost completely removed by this process, it is obviously legitimate to weigh the residue obtained by evaporating the aqueous extract of the reduced cobalt, and thus to obtain directly the amount of impurity present in the metal. This difference of procedure in the two cases is an interesting example of the way in which subordinate side reactions may influence two researches otherwise unusually analogous.

In the next four analyses (5 to 8) the cobalt was leached with the purest hot water in a platinum dish and the solution, after filtration, was evaporated to dryness. The residue was taken up with water, filtered from the deposited cobaltic hydroxide into a weighed platinum crucible, again evaporated, heated to 130° , and weighed. That these residues contained

cobalt was undoubtedly true from the fact that they were colored a pale blue both after evaporation and after heating. During the heating however a slight blackening took place which was due to the oxidation of traces of unoxidized cobaltous hydrate. In order to make sure that all unreduced bromides had been removed from the cobalt by the process of leaching, in each analysis the metal was dissolved by cold very weak nitric acid* and treated with silver nitrate. As not even the faintest cloudiness was ever again visible in these solutions, it was assumed that the soluble matter had been completely removed.

In analysis 5 the bromine in the residue was determined and the result found to be considerably too low to correspond with the weight of the residue, if calculated as sodium bromide. In order to discover the cause of this discrepancy an elaborate series of experiments was carried out at the expense of much time and labor. To describe these experiments in full would result only in confusing the mind of the reader. It is sufficient to say that pure spongy cobalt was treated with varying amounts of pure sodium bromide in solution, the conditions being regulated so as to be as nearly as possible like those in the analyses. The following conclusions drawn from these experiments are of great importance.

In the first place, no bromine is lost by the residues either during evaporation or in heating to 130°. The cobalt in the residues may be present in three forms, as cobaltous hydrate which has escaped oxidation, as cobaltic hydrate, and as unreduced cobaltous bromide,† each in exceedingly small amounts. The doubt as to the quantity of each present makes it impossible to apply the correction for dissolved cobalt with any degree of accuracy and in the table of results no attempt has been made to do so. In the later analyses this cause of uncertainty was removed.‡ This correction within a correction is however an infinitesimal of the second order; neglecting it can produce no serious effect upon the accuracy of the final result.§ In this respect the research upon cobalt differs from that upon nickel, where the amount of hydroxide in the residue was relatively great, owing to the fact that it had not been chiefly eliminated by oxidation during the evaporation.

* In a platinum dish this solution takes place with great ease, and with no danger of a loss of bromine. The galvanic action is a great assistance.

† Cobaltous bromide could only have found its way into this residue by having been protected from reduction by enclosure in crystals of sodic bromide. It must have been exceedingly small in amount, if present at all.

‡ Compare page 363.

§ This extra cobalt may partly explain why the sum of the total analysis slightly exceeds 100.000 per cent. See page 365.

The possibility of the presence of some other acid than hydrobromic acid in the residues led us to make tests in this direction. Silicic acid was of course the first one to suggest itself. Early in the work one test had been made by subliming about two grams of pure cobaltous bromide from a platinum boat in a current of hydrobromic acid gas. After the sublimation of the bromide the boat was perfectly bright, and gave not the slightest evidence of the presence of any silica. One of the residues was now treated with pure strong hydrochloric acid, heated to 130° , again treated with hydrochloric acid, and filtered. The amount of silica found, three one-hundredths of a milligram, is a negligible quantity. Although the purity of the phosphoric anhydride used for drying our gases had been proven by passing air through a tube filled with the pentoxide into aqua regia, which upon evaporation gave no precipitate with ammoniac molybdate, nevertheless one of the soluble residues from the reduced cobalt was tested with the same reagent with a negative result.

Upon examining one of the earlier residues for sulphuric acid, however, a slight precipitate of baric sulphate was formed. The source of this sulphuric acid was hard to discover, but finally it was found that the strong sulphuric acid in some of the drying columns had become discolored in places by organic matter. This must have led to a slight decomposition of the acid and formation of sulphur dioxide, which was subsequently oxidized to sulphuric acid by the bromine. The amount of sulphuric acid present in the bromide was very small, 3.88 grams of cobaltous bromide giving only 0.00036 gram of baric sulphate in one case. As in the instance of nickel, however, this cause of error was wholly eliminated in the later experiments, and no trace of sulphuric acid could be detected in the material used in the last series.

The conclusions to be drawn from these experiments seem to be :—

First, that our cobaltous bromide was almost if not completely reduced.

Secondly, that the impurities, which consist of alkaline bromides (with, in some cases, a minute trace of sulphates), can be completely removed by leaching the cobalt.

Thirdly, that the residue obtained by evaporating the water extract of the cobalt after reduction represents within an exceedingly small amount the weight of the impurities.

In the fourth series, during which the truth of this third conclusion was not realized, and a method similar to that used in the nickel research was adopted, the weight of the residue had to be calculated. The basis of calculation was the knowledge obtained from analysis 5, Series V. Unfortunately this is the only analysis of material similar to that used in

Series IV., where both the weight of the residue and the silver bromide obtained from it were determined. Since, however, the use of this analysis causes the average of Series IV. to approach within one part in thirty thousand of the average of Series V. and VI., we may safely assume that the rather meagre data represent with great exactness the real weight of the impurity contained in this Sample I. of cobaltous bromide. In Series V. and VI. the residues were weighed directly, so that this factor was not needed. Below are given the results of the first two series of analyses.

THE ATOMIC WEIGHT OF COBALT.

O = 16 ; Br = 79.955.

FOURTH SERIES (PRELIMINARY). $\text{CoBr}_2 : \text{Co}$.

No. of Anal.	Sample of CoBr_2 .	Observed Weight of Cobaltous Bromide in Vacuum.	Observed Weight of Cobalt in Vacuum.	Weight of AgBr found from Residue.	Weight of Residue calculated from AgBr.*	Atomic Weight of Cobalt.
		grams.	grams.	grams.	grams.	
1	I.	5.59216	1.50873	0.00309	0.00193	59.007
2	I.	4.61944	1.24807	0.00681	0.00426	58.996
3	I.	3.75291	1.01713	0.01267	0.00793	58.989
4	I.	3.00645	0.81409	0.00815	0.00510	59.007
Average . .						59.000

FIFTH SERIES. $\text{CoBr}_2 : \text{Co}$.

No. of Anal.	Sample of CoBr_2 .	Observed Weight of Cobaltous Bromide in Vacuum.	Observed Weight of Cobalt in Vacuum.	Weight of Residue.	Corrected Weight of Cobaltous Bromide.	Corrected Weight of Cobalt.	Atomic Weight of Cobalt.
		grams.	grams.	grams.	grams.	grams.	
5	I.	5.32955	1.44189	0.00761*	5.32194	1.43428	58.996
6	I.	7.51430	2.02965	0.00644	7.50786	2.02321	58.989
7	II.	2.32910	0.62957	0.00280	2.32630	0.62677	58.973
8	II.	7.45336	2.01378	0.00642	7.44694	2.00736	59.011
Average . .							58.992

* From the residue in Series V., analysis 5, was obtained 0.01216 gram of

It seemed highly important to us at this point to prepare cobaltous bromide which should be free from every impurity. In the first place the drying apparatus was slightly modified, no strong sulphuric acid being used except in drying the air necessary for sweeping the nitrogen out of the weighing bottle. Dilute sulphuric acid was substituted in every case, and two columns of stick potash followed by one of phosphoric anhydride were inserted beyond this dilute acid. As the porcelain tubes had evidently been the source of the alkaline impurities found, a platinum lining, made by bending a large piece of platinum foil into the form of a cylinder, was provided for the outside porcelain tube.* The smaller porcelain tube was not used at all, the sublimed material being removed by taking out the foil and unfolding it. Cobalt from Sample III. was then sublimed in the remodelled apparatus from a platinum boat. The material obtained in this way gave results for the atomic weight altogether too high, a circumstance due to large quantities of platinum actually found in the sublimed bromide. Even here a small amount of alkaline impurity existed, having crept in through the crack in the platinum foil. Hence, no more work was done with this material; but renewed precautions were taken to prepare by the older method cobaltous bromide which should contain the smallest possible number and quantity of impurities.

Four analyses were made with this new material, which proved in spite of all our care to contain as much soluble matter as before. The water extracts from these analyses were evaporated in a flat platinum dish, which exposed a large surface of the solution to the air. This served to oxidize completely the dissolved cobaltous hydrate, for the residues did not become gray when heated, and upon the addition of water gave perfectly clear solutions. These residues were faintly blue, the color being due doubtless to a trace of unreduced cobaltous bromide. For some undiscovered reason, the amount of silver bromide obtained from the residues was still too small to correspond to the weight of the residue, if calculated as sodic bromide.

Tests were repeated for sulphuric, phosphoric, and silicic acids with the greatest possible care, but still with negative results. In one analysis the cobalt was determined in the residue and found to be only 0.00013 gram. It is possible, however, that these few tenths of a milligram dis-

argentic bromide. Hence 0.0010 gram of argentic bromide corresponds to 0.000626 gram of residue. This factor is used in calculating the results in Series I.

* Compare the preceding paper on Nickel, page 331.

Weight of Residue.	Weight of AgBr obtained from Residue.	NaBr in Residue, calculated from AgBr.	Unidentified.
grams. .00306	grams. .00439	grams. .00240	grams. .00066
.00643	.00978	.00536	.00107

crepancy are due to the presence of all or at least several of the above mentioned acids combined with sodium, each in quantity too minute for detection; and for the present this will have to rest as the explanation.

SIXTH SERIES. CoBr_2 : Co.

No. of Anal.	Sample of CoBr_2 .	Observed Weight of Cobaltous Bromide in Vacuum.	Observed Weight of Cobalt in Vacuum.	Weight of Residue.	Corrected Weight of Cobaltous Bromide.	Corrected Weight of Cobalt.	Atomic Weight of Cobalt.
9	III.	grams. 5.11197	grams. 1.38027	grams. 0.00306	grams. 5.10891	grams. 1.37721	59.016
10	III.	6.41822	1.73333	0.00483	6.41339	1.72850	58.999
11	III.	6.60707	1.78778	0.00902	6.59805	1.77876	59.021
12	III.	3.03497	0.82249	0.00643	3.02854	0.81606	58.982
Average . .							59.004

Average of Series V. and VI. . . Co = 58.998.

This final average differs from that published before by only about one part in ten thousand; but in comparing the two one must remember that the material used last year must have been contaminated by the same impurities which have been discussed in this paper. If the impurity contained as much bromine as cobaltous bromide contains, it would have had no effect upon last year's results. In the case of *nickel*, where the impurity consisted wholly of sodic bromide, the effect of correcting the observed results in the paper of 1897 was to raise the atomic weight of nickel from 58.688 to 58.703. The impurity from our *cobaltous* bromide, on the other hand, contained unknown substances in quantities so small as to elude detection, but large enough to change the sign of the corresponding correction. Thus 22.63 grams of cobaltous bromide in Series V. (the series in which the materials most nearly

resembled those used in Series II. and III. of last year's work) were found to contain 0.02327 gram of impurity. If, as we may reasonably suppose, all the residues obtained from this sample of material resembled that found in analysis 5, Series V., this residue would have yielded 0.0372 gram of argentic bromide. We may now correct last year's results by subtracting from the several weights of cobaltous bromide proportional weights of impurity, and also subtracting from the several weights of argentic bromide amounts of this substance corresponding to the impurity. Making this correction, the atomic weight of cobalt would be *lowered* 0.008, the averages of Series II. and III. becoming 58.987 and 58.979. Our uncertainty regarding the nature and amount of the impurity thus involves an uncertainty of about one part in six thousand in last year's results. In the light of all the circumstances, it is perhaps safest not to attempt any correction of these values, but to accept them uncorrected as subject to this possible error. The results are accordingly given below in an uncorrected form.

The data just discussed obviously afford a basis for recording the total percentage composition of the cobaltous bromide analyzed.

COMPLETE ANALYSIS OF COBALTOUS BROMIDE.

BASED UPON SERIES II., III., AND V.

	Per cent.	
Cobalt (Series V.)	= 26.923	
Total Bromine $\left\{ \begin{array}{l} \text{(II.) } 73.050\% \\ \text{(III.) } 73.053\% \\ \text{Aver. } 73.051\% \end{array} \right\} = \left\{ \begin{array}{l} \text{Bromine combined} \\ \text{with Cobalt} \end{array} \right\} =$	72.981	
	$\left\{ \begin{array}{l} \text{Bromine actually} \\ \text{found in impurity} \end{array} \right\} =$.070
Total impurity . . = 0.103% = $\left\{ \begin{array}{l} \text{Remainder of} \\ \text{impurity} \\ \text{(chiefly Sodium)} \end{array} \right\} =$.033	
Total	= 100.007	

Series VI., perhaps the best of all, is not included in this table because the material used in it was not quite identical with that used in the three other series. Obviously it is possible to calculate two more ratios involving the atomic weight of cobalt, in which the values for the *bromine* in the bromide are compared with the *cobalt* found in it. Into this calculation the weight of the bromide itself enters simply as a constant, and an indifferent impurity (such as water) would be eliminated from the

result. The table below includes all of the five possible ratios obtainable from our work, series I. and IV. being rejected because they were merely preliminary:—

2 AgBr	:	CoBr ₂ (Series II.)	58.995
2 Ag	:	CoBr ₂ (Series III.)	58.987
CoBr ₂	:	Co (Series V. and VI.)	58.998
2 AgBr	:	Co (Series II. and V.)	58.994
2 Ag	:	Co (Series III. and V.)	58.992
Average			<u>58.993</u>

This table, although giving an interesting statement of the possible combinations, does not yield a fair average, — for Series V. is introduced three times, Series II. and III. each twice, while Series VI., which is at least as accurate as the others, appears only once. A fairer method would probably be to avoid all hypotheses and combinations, and assign to each of the four series equal weight, as follows:—

Series II. (uncorrected)	Co	=	58.995
Series III. (uncorrected)	Co	=	58.987
Series V. (corrected)	Co	=	58.992
Series VI. (corrected)	Co	=	59.004
Final Average . . .			<u>58.995</u>

Obviously it makes but little difference which method we adopt: the averages are essentially identical. The highest individual experimental result among all these determinations was 59.021, and the lowest 58.955, the average variation from the mean 58.995 being 0.012. Because these results are less concordant than one could wish, and the conclusion is somewhat less positive than that reached in the case of nickel, the atomic weight of cobalt is being further studied by radically different methods in this Laboratory.

In a recent article,* Professor Winkler calls attention to some possible errors, in the work upon both nickel and cobalt published last year. That the disagreement between his results and ours is due to the methods employed by him in his work upon these two elements has been sufficiently shown in the preceding paper upon the atomic weight of nickel. In addition, however, his several suggestions concerning our own work should obviously be reviewed and discussed in detail.

His specific criticisms are four in number. First, he suggests that the

* Zeitschr. Anorg. Chem., XVII. 236.

porcelain tubes might have been attacked during the sublimation of the bromides, with the introduction of foreign bromides into the nickelous and cobaltous bromides. He goes on to state that the bromides were dried in an acid atmosphere, and probably retained hydrobromic acid after this gas had been displaced by air. His third criticism is that the nickelous bromide in the earlier analyses contained nickelous oxide which had to be determined and subtracted; and his final objection applies to the use of the Gooch crucible.

Answers to the greater part of his criticisms can be found in the very articles which he criticises. In one case only can his view be substantiated;—the porcelain tubes are really attacked. That this flaw was a possibility we realized at the time; but we also realized the smallness of the error introduced by even a comparatively large amount of such impurity. This matter has been already discussed in detail, both in this paper and in the paper upon the atomic weight of nickel.

There are two possible ways in which hydrobromic acid could have been retained:—by adsorption and by inclusion. At the high temperatures employed the adsorption must have been very slight, and the long process of washing with an indifferent gas was favorable to the elimination of any tendency in that direction. While the inclusion of *liquids* is a very serious possible cause of error, that of *gases* is usually negligible because of the small mass involved. For this reason crystallization from solutions is far less satisfactory than sublimation as a means of purification.

That as a matter of fact our bromides were neutral there is no lack of evidence. The possibility of acidity had occurred to us also, but reasoning from analogy we had decided that this possibility was rather an improbability. Bromides and chlorides of barium and strontium, heated in the same way in a dry acid atmosphere, after the acid has been displaced by dry air, give absolutely neutral reactions with methyl orange.* With cobaltous bromide the end point is not as easy to detect as with the before mentioned halides on account of the color of the dissolved salt, but colorimetric comparison makes it possible to distinguish the change very accurately. A solution of our cobaltous bromide containing methyl orange perceptibly changed color upon the addition of the minimum amount of hundredth normal acid necessary to produce a change of color in pure water containing methyl orange, showing that the salt must have been very near if not at the turning point. As a final test, potassium

* These Proceedings, XXIX. 59, XXX. 373.

bromide was sublimed in the apparatus which had been used for the preparation of the cobaltous bromide. The sublimate was then heated in a current of dry nitrogen and hydrobromic acid gas, and finally, when cool, the nitrogen and acid were displaced by dry air, just as in preparing the cobaltous bromide for analysis. This potassic bromide upon solution gave an absolutely neutral reaction with methyl orange. Taking into consideration these three points, one cannot believe that enough hydrobromic acid was retained to have had an appreciable influence on our results.

The third criticism, objecting to the fact that in some analyses a small amount of nickelous oxide was found in the bromide, is an unfortunate one. A careful perusal of the work would have shown that only in the preliminary series of results was this the case, and that this series does not enter into the final average, although its results differ only by a very small amount from those subsequently obtained with material free from oxide. As far as the nickel is concerned, a conclusive proof of the absence of acid is afforded by this very fact that the earlier determinations, in which it was necessary to filter off a residue of finely divided nickelous oxide, gave results no higher for nickel than the later results.* Hence the second and the third criticisms are obviously inconsistent with one another.

The advantages of the Gooch crucible are too well known to need mention. Professor Winkler's specific objection to the collecting of displaced asbestos upon an ordinary filter affects only an amount of a few tenths of a milligram; and a proof that no error was introduced in this way lies in the fact that in every case the amount of silver bromide found agreed very closely with the amount of silver necessary to complete the reaction, where all but a few tenths of a per cent of the silver was weighed out, and the remainder was added volumetrically. The following brief table will make this clear.

Thus, in the cobalt work, 18.16302 grams of silver yielded 31.61642 grams of silver bromide, — a ratio of 57.448 to 100.000, — while in the case of nickel, 15.51556 grams of bromide gave 26.67078 grams of silver bromide, — a ratio of 57.444 to 100.000, while Stas found 57.445.

From the cobalt work	AgBr : Ag = 100.000 : 57.448
From the nickel work	AgBr : Ag = 100.000 : 57.444
From Stas's work	AgBr : Ag = 100.000 : 57.445

* The slight colloidal solubility of nickelous hydroxide was evidently destroyed by the presence of large amounts of nickelous bromide, as one would expect.

Thus the last of Professor Winkler's criticisms is sufficiently answered.

After necessarily dwelling at such length upon disagreements, it is a pleasure to emphasize other points in which we agree with Professor Winkler. The evidence of our work, together with Dr. Cushman's, strongly supports Winkler's contention that nickel and cobalt, as we knew them of old, cannot contain more than an infinitesimal amount of any unknown element. Several radically different methods of preparation and many fractionations invariably led us to constant atomic weights, within a reasonable limit of experimental error; and we are forced to conclude that the familiar properties of these common and useful metals are to be ascribed to elements as definite as any of the seventy-five. It is needless to point out also that we agree with Professor Winkler in assigning to cobalt a higher atomic weight than to nickel, in spite of the conflict of periodicity with rhodium and palladium. According to our results, the atom of cobalt, weighing almost exactly 59.00, is very nearly half of one per cent heavier than that of nickel.

CAMBRIDGE, October 29, 1898.